



NATO ARW - METALLIC MATERIALS WITH HIGH STRUCTURAL EFFICIENCY  
Kyiv, Ukraine, 7-13 September 2003

# NANOSTRUCTURED AND NANOCOMPOSITE LIGHT-METAL BASED COMPOUNDS FOR HYDROGEN STORAGE

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# **HYDROGEN – THE FUEL OF THE FUTURE**

With the concerns of the global climate warming it is absolutely indispensable for the mankind to develop new clean energy sources other than **fossil fuels**.

The consensus of opinion is setting on **hydrogen** for either supplying **fuel cells** or **internal combustion** engines as the way forward. According to many in the scientific community we are now at the verge of a **new hydrogen age**. Extensive research efforts are laying down the foundation of the next **industrial revolution** in the application of hydrogen as the fuel of the future.

# **HYDROGEN STORAGE FOR PROTON MEMBRANE EXCHANGE (PEM) FUEL CELLS FOR VEHICULAR (MOBILE) APPLICATIONS**

Excerpts from Ritter et al, *Materials Today*, September 2003, pp.18-23

“In recent years, months, weeks, and even days, it has become increasingly clear that hydrogen as an energy carrier is “in “ and carbonaceous fuels are “out”. The hydrogen economy is coming with the impetus to transform our fossil energy-based society, which inevitably will cease to exist, into a renewable energy-based one.

However, hydrogen **storage** is proving to be one of the most important issues and potentially biggest roadblock for the implementation of a hydrogen economy. Of the three options that exist for storing hydrogen, in a **solid**, **liquid** and **gaseous** state, the former is becoming accepted as the only method potentially able to meet the gravimetric and volumetric densities of the recently announced FreedomCar goals; and of all known hydrogen storage materials, **complex hydrides may be the only hope”**.

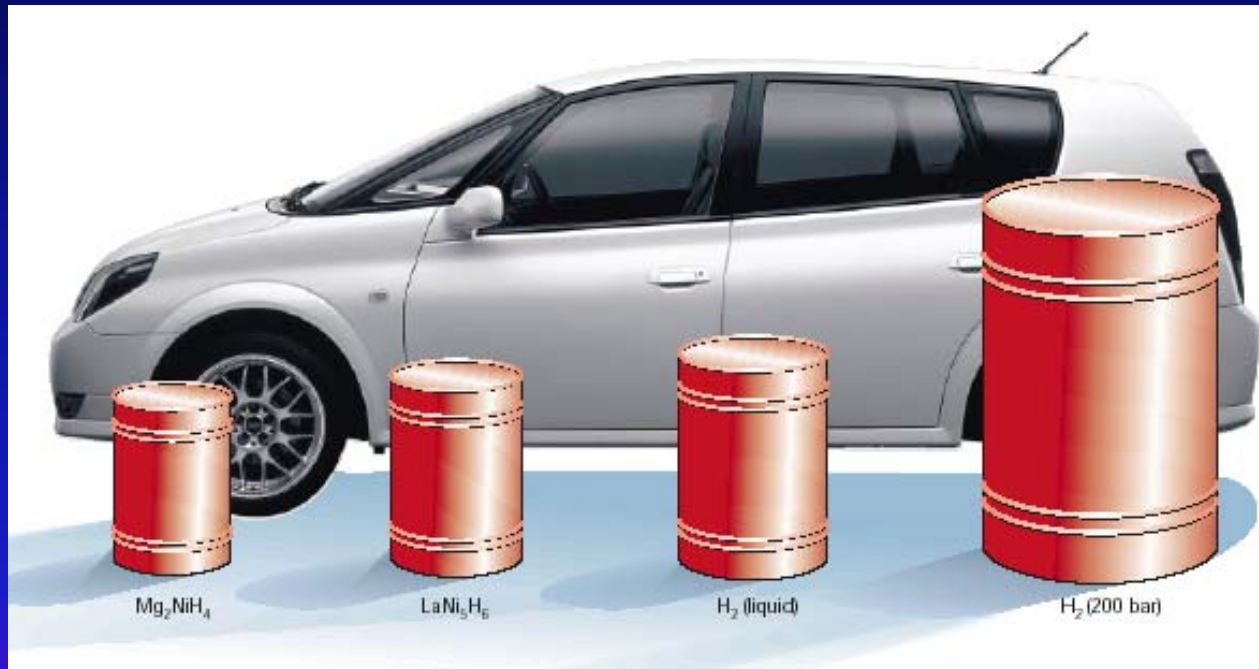
# **HYDROGEN** STORAGE FOR *PEM* FUEL CELL-POWERED VEHICLES

The highest *volumetric* density required

| Storage system                                     | Volumetric density<br>(kgH <sub>2</sub> m <sup>-3</sup> ) | Drawbacks  |
|--|---|--|
| Compressed hydrogen gas under 80 MPa pressure      | ~40   | Safety problems<br>(enormous pressures required) |
| Liquid hydrogen at cryogenic tank at -252°C (21K): | ~71   | Large thermal losses<br>(open system!)           |
| Solid metal/intermetallic hydrides                 | ~80-150   | None   |

# HIGH VOLUMETRIC HYDROGEN DENSITY FOR VEHICLES

~4 kg of hydrogen → range ~480 km (300 miles)



Volume of 4 kg of hydrogen compacted in different ways, with  
size relative to the size of a car

Toyota press, 33rd Tokyo Motor Show, 1999; L.Schlapbach and A.  
Züttel, Nature, 414, 353-358 (2001)

# **HYDROGEN** FOR *PEM* FUEL CELLS-

## Gravimetric density

The highest *gravimetric* density: **light metal-based hydrides**

| Metal-hydrogen system | Hydride  | Theoretical hydrogen capacity (wt%) | Density of hydride (g/cm <sup>3</sup> ) | Decomposition temperature (°C) |
|-----------------------|--|-------------------------------------|---|--------------------------------|
| Li-B-H                | LiBH <sub>4</sub>  | 18.4                                | 0.67                                    | 380                            |
| Mg-B-H                | Mg(BH <sub>4</sub> ) <sub>2</sub> or MgB <sub>2</sub> H <sub>8</sub> | 15.3                                | 0.99                                    | 300-800 (?)                    |
| Na-B-H                | NaBH <sub>4</sub>  | 10.6                                | 1.07                                    | 400                            |
| Mg-Fe-H               | Mg <sub>2</sub> FeH <sub>6</sub>                                     | 5.4                                 | 2.72                                    | 320                            |
| Mg-Mn-H               | Mg <sub>3</sub> MnH <sub>7</sub>                                     | 5.2                                 | 2.30                                    | 280                            |
| Mg-Co-H               | Mg <sub>2</sub> CoH <sub>5</sub>                                     | 4.5                                 | 2.70                                    | 350 (?)                        |

# **HYDROGEN FOR *PEM* FUEL CELLS-**

## **Requirements for metal/intermetallic hydrides**

- **World Energy Network (Japan):**

**Hydrogen capacity > 3wt%; desorption temp.  $\sim 100^{\circ}\text{C}$ ;  
5000 cycles life**

- **International Energy Agency:**

**Hydrogen capacity > 5wt%; desorption temp.  $< 150^{\circ}\text{C}$ ;  
1000 cycles life**

- **Department of Energy (USA):**

**Hydrogen capacity > 6wt%**



# **HYDROGEN FOR *PEM* FUEL CELLS-** **Metal/intermetallic hydrides-Conclusions**

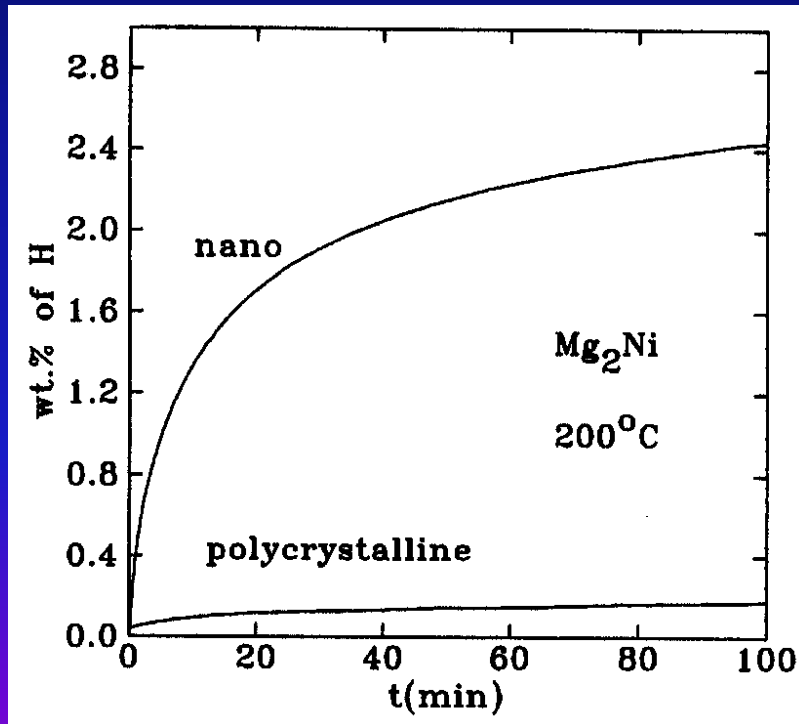
- All light metal-based hydrides have excellent hydrogen storage capacities sometimes exceeding those required by various agencies for vehicular applications
- All of them have a fatal drawback: **too high desorption temperature!**
- Their desorption **kinetics are slow** for polycrystalline alloys

**HOW CAN WE IMPROVE KINETICS AND  
DESORPTION TEMPERATURE ?!**

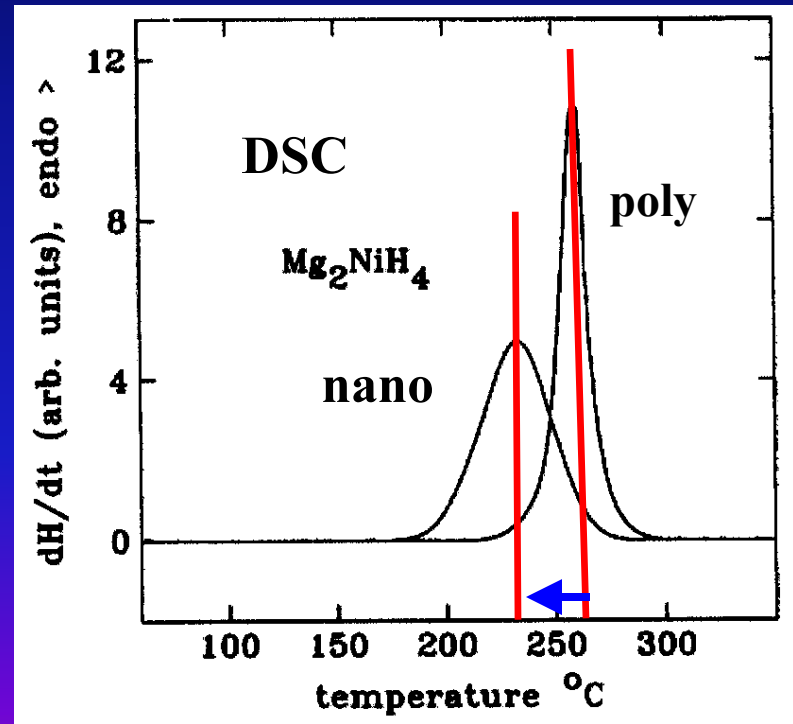
# BEHAVIOR OF NANOSTRUCTURED/NANOCOMPOSITE HYDRIDES

Zaluska et al., Appl. Phys. A 72 (2001) 157-165 (review paper)

## Absorption kinetics



## Desorption temperature



# METHODS OF SYNTHESIS OF NANOSTRUCTURED/NANOCOMPOSITE HYDRIDES

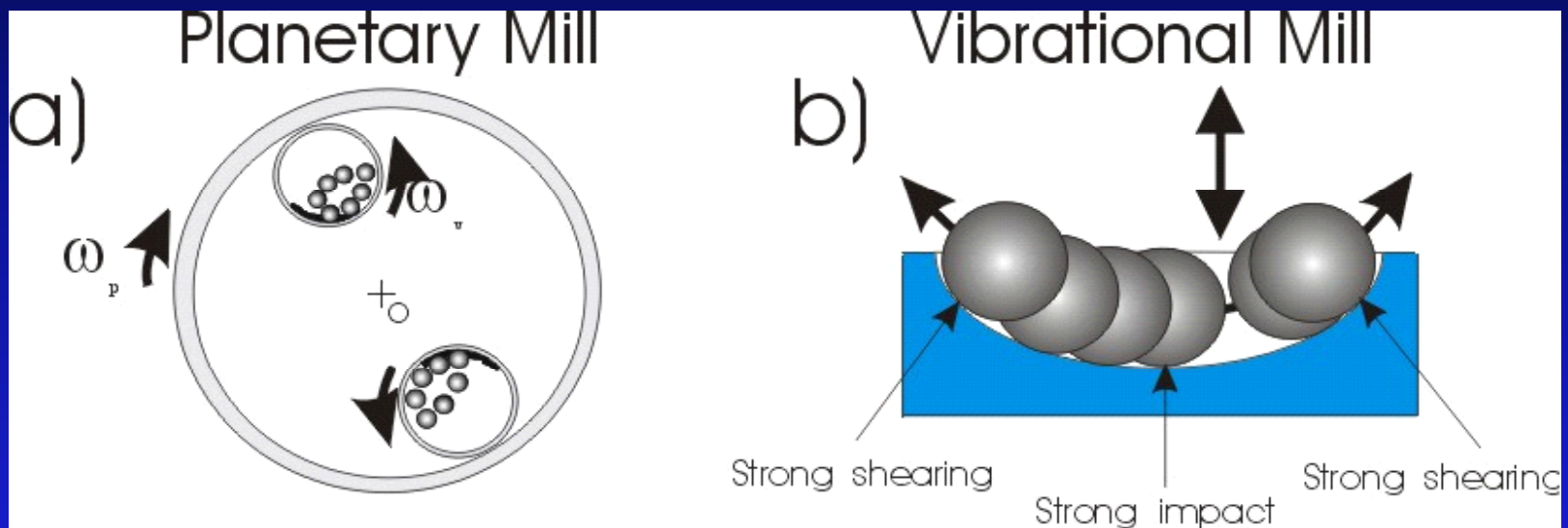
**Definition:** *Nanostructured/nanocomposite* means that each phase present in the individual powder particle is in the form of *grains* with *nanometer* size; one particle is one *nano-polycrystal*

**1.Two-step:** mechanical alloying (MA) of elemental metal powders or milling (MM) of bulk alloys under protective gas (Ar, He) ; subsequent **hydrogenation** in a **separate step** under appropriate pressure of  $H_2$

**2.One-step:** mechanical alloying/milling of elemental metal powders/bulk alloys **directly under hydrogen** – Reactive Mechanical Alloying/Milling (RMA/RMM) – cost reduction and ease of hydride formation - **preferable**

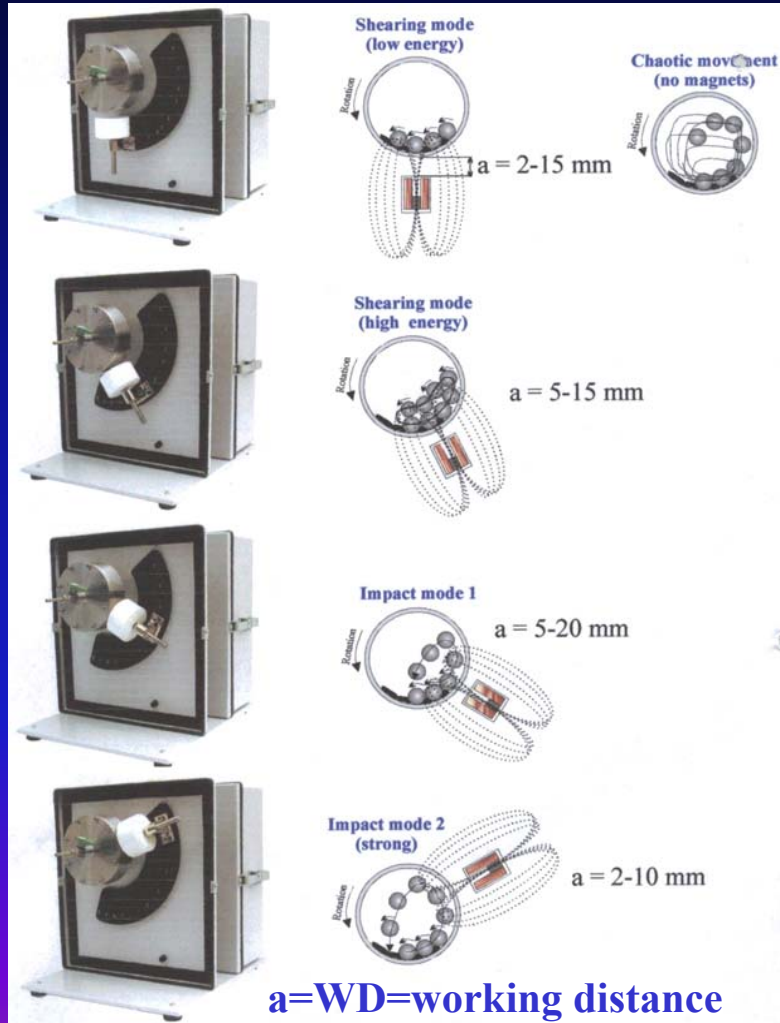
# METHODS OF SYNTHESIS OF NANOSTRUCTURED/NANOCOMPOSITE HYDRIDES-cont

## Common milling techniques



**Drawback:** completely uncontrolled (chaotic)  
movement of grinding balls

# CONTROLLED REACTIVE MECHANICAL ALLOYING/MILLING (CRMA/MM)



**Magneto-mill Uni-Ball-Mill 5 for controlled milling - trajectories of milling balls are controlled by strong NdFeB magnets**

Courtesy of A.O.C. Scientific Engineering, Australia

# Mg-M-H SYSTEMS SELECTED FOR SYNTHESIS BY CRMA

Mg-2B (crystalline)(c)-H



Mg-2B (amorphous)(a)-H

2Mg-Co-H



3Mg-Mn-H



2Mg-Fe-H



**Complex metal hydrides:** mixed ionic-covalent bonding  
between metal and hydrogen complex, e.g.  $(\text{FeH}_6)^{4-}$

# EXPERIMENTAL OUTLINE-Milling

1. Elemental powders of Mg, B (cryst&amorph.), Co, Mn and Fe.
3. Handling of powders in the glove bag filled with helium for environmental protection.
4. Milling in the magneto-mill Uni-Ball-Mill 5; ball-to-powder weight ratio (BPWR) was 10:1 for the 2Mg-Co and 3Mg-Mn mixtures and ~40:1 for the other mixtures.
3. Hydrogen pressure in the milling vial 400-500 kPa
5. Working distance WD= 10 to 3 mm depending on the specific alloy; it governs the force of the magnetic attraction exerted onto the steel balls.

# **EXPERIMENTAL OUTLINE-**

## **Microstructural and thermal studies**

- **High-resolution field emission SEM (FE SEM) LEO 1530 with integrated EDAX Pegasus 1200**
- **X-ray diffraction (XRD) using Philips PW 1730 and Siemens D500 diffractometers; CuK $\alpha$  radiation ( $\lambda=0.15418$  nm)**
- **Differential scanning calorimetry (DSC) (Netzsch 404); heating rate 4 K/min; argon flow rate 16ml/min**
- **Thermogravimetric analysis (TGA)(TA Instruments); heating rate 10 K/min; helium flow**



# EXPERIMENTAL OUTLINE-

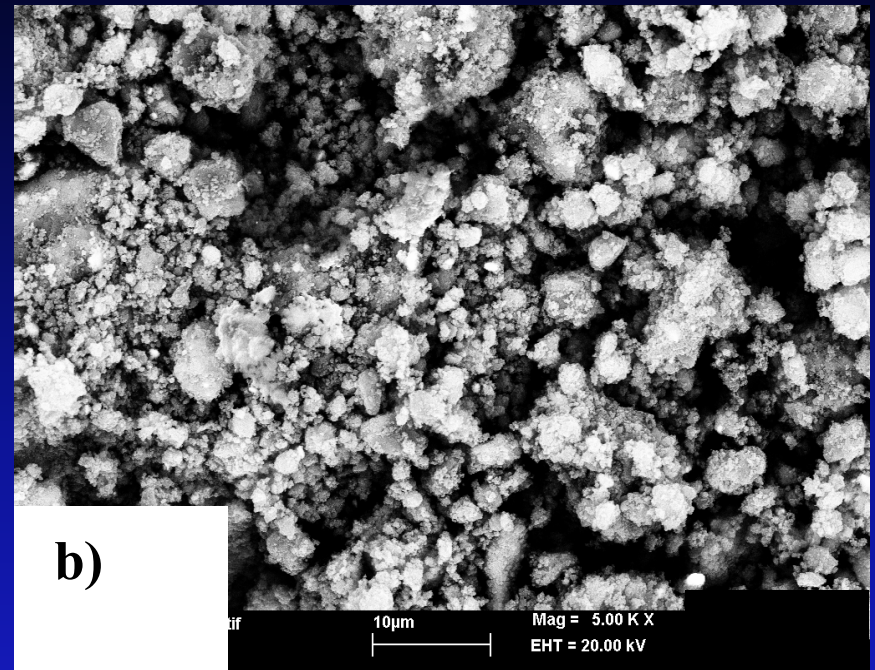
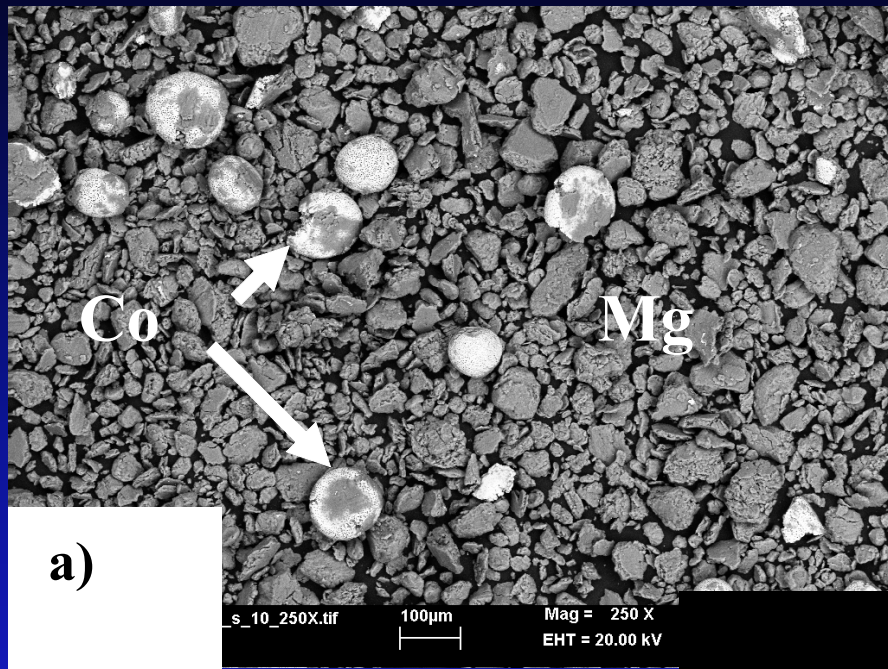
## Nanograin size calculations

From **XRD peak broadening** using linear regression procedure (Klug&Alexander, X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials, John Wiley & Sons, New York (1974)).

$$\frac{\delta^2(2\theta)}{\tan^2 \theta} = \frac{K\lambda}{L} \left( \frac{\delta(2\theta)}{\tan \theta \sin \theta} \right) + 16e^2$$

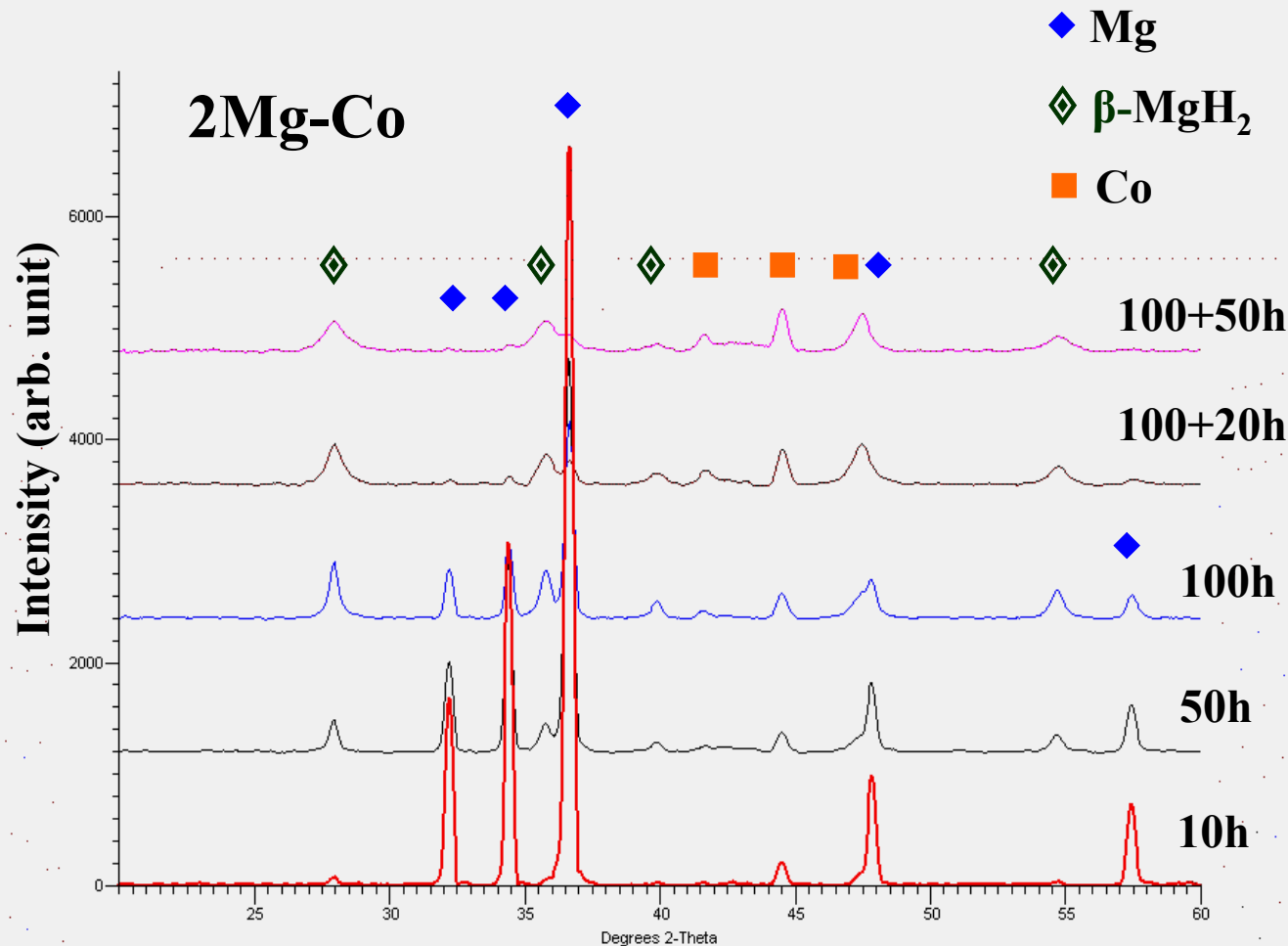
L-nanograin (crystallite) size; e-lattice strain;  $\lambda$ -the wave length;  $\theta$ -position of the analyzed XRD peak maximum; K-constant;  $\delta(2\theta)=B(1-b^2/B^2)$ (rad)-the instrumental broadening-corrected “pure” XRD peak profile breadth; B and b-FWHM (full width at half maximum) of analyzed and reference peak, respectively

# RESULTS-Microstructure of powders



Backscattered electron (BSE) images of the morphology of powders processed under shearing mode by CRMA under hydrogen. **a)** **2Mg-Co** mixture milled for **30h** using WD=10 mm and BPWR=10:1 and **b)** **Mg-2B (crystalline (c) boron)** mixture milled for **5h** using WD=5 mm and BPWR=44:1. RPM=60 applied during milling.

# RESULTS – XRD patterns vs. milling time



Typical for

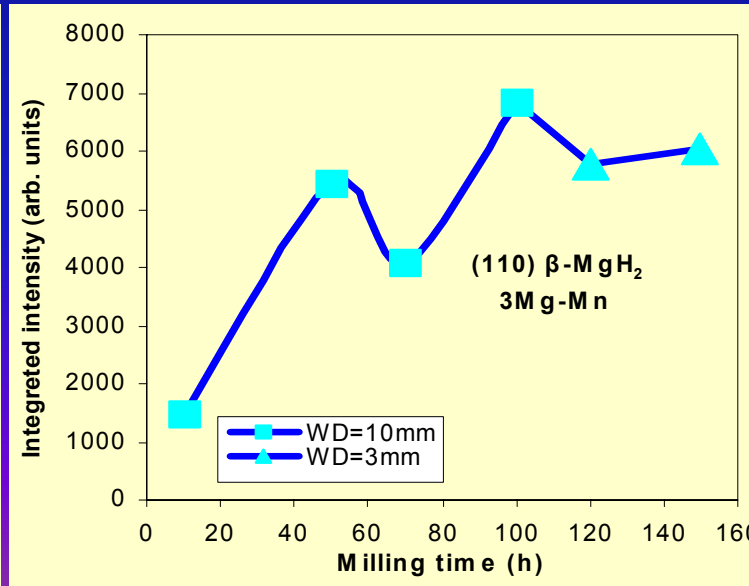
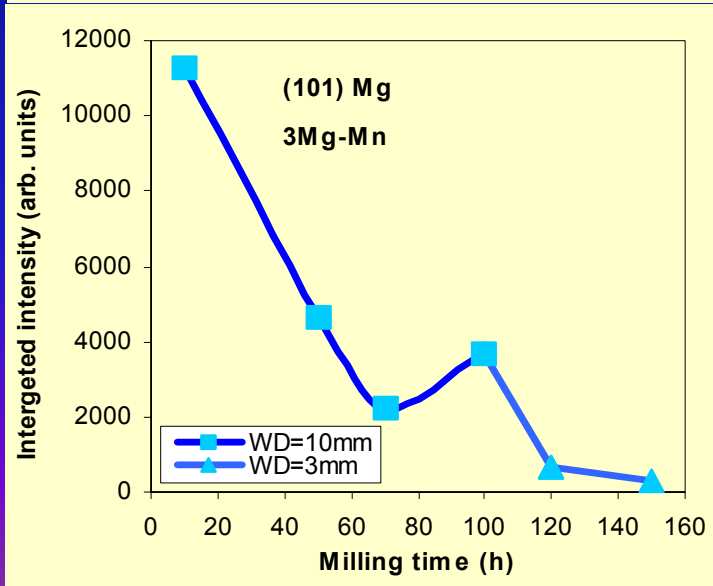
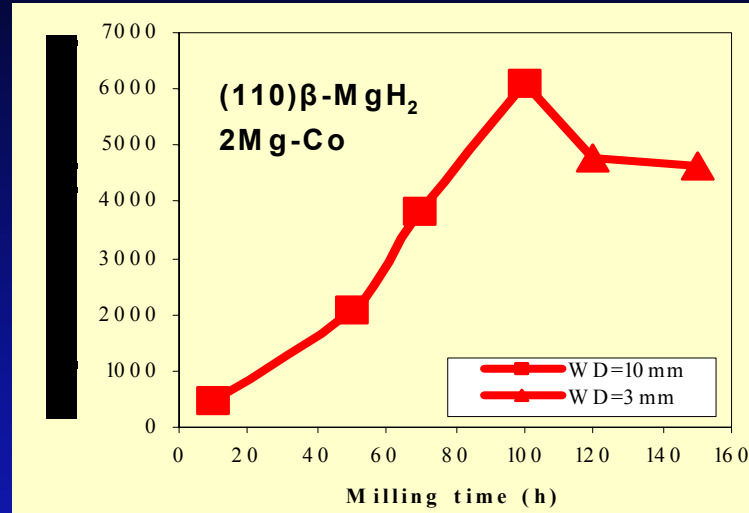
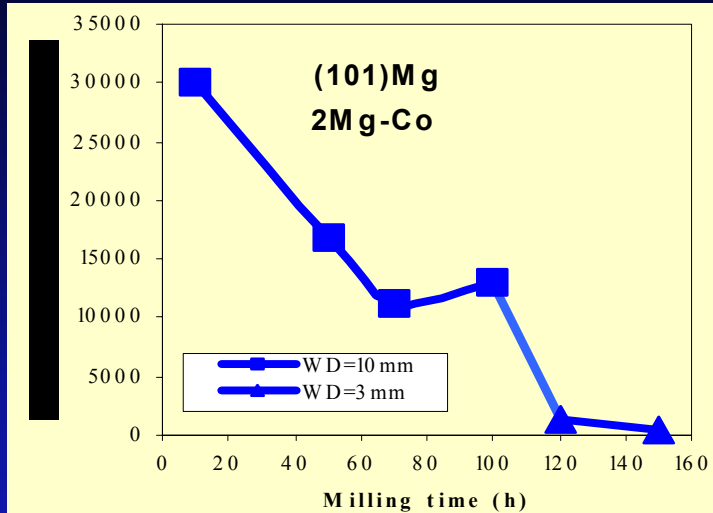
**2Mg-Co**

**Mg-2B**

**3Mg-Mn**

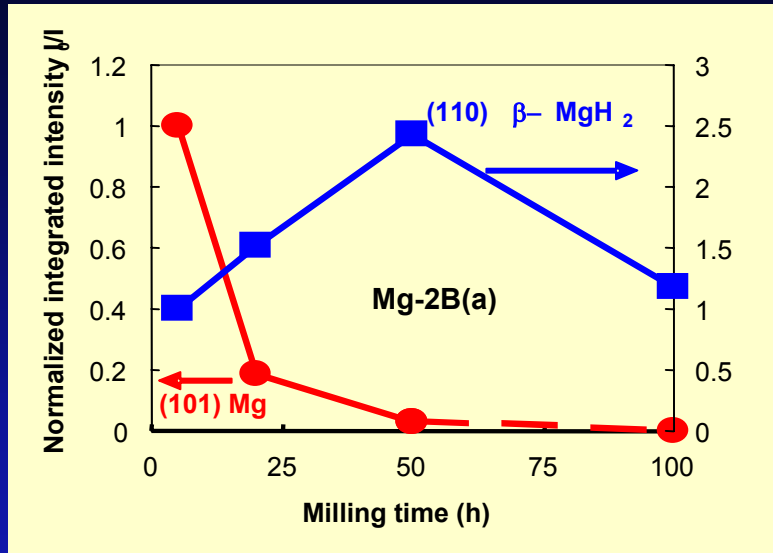
systems

# RESULTS- XRD intensities vs. milling time

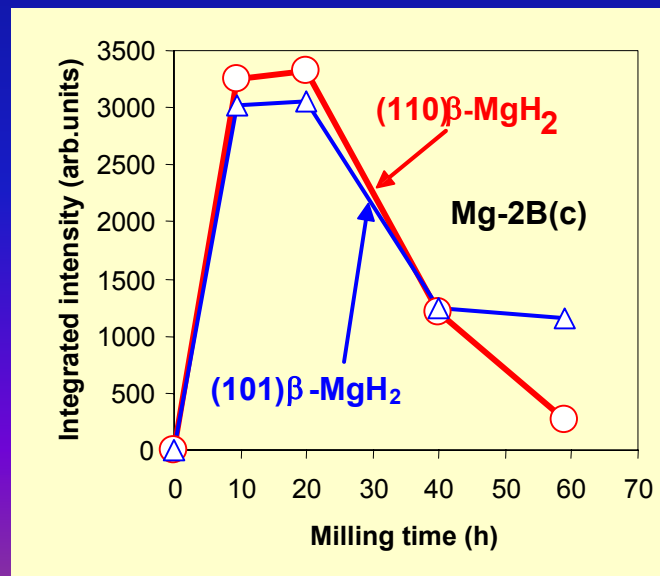
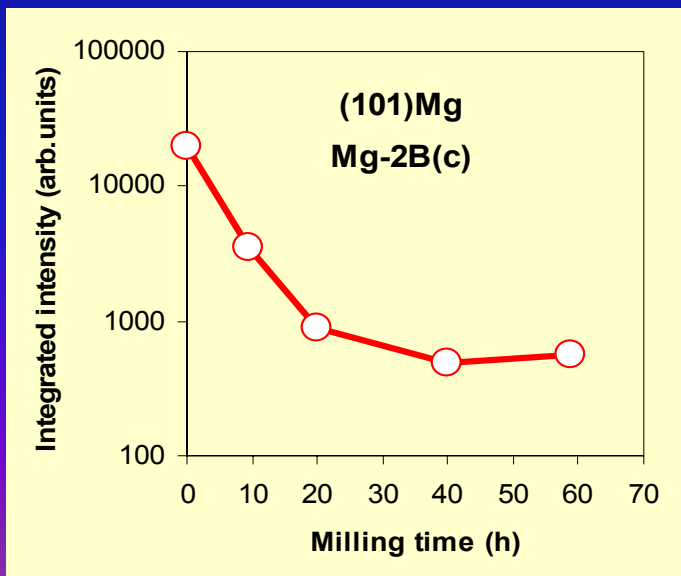


Mg  
consumed  
almost  
completely  
to form  
β-MgH<sub>2</sub>  
in  
2Mg-Co  
3Mg-Mn

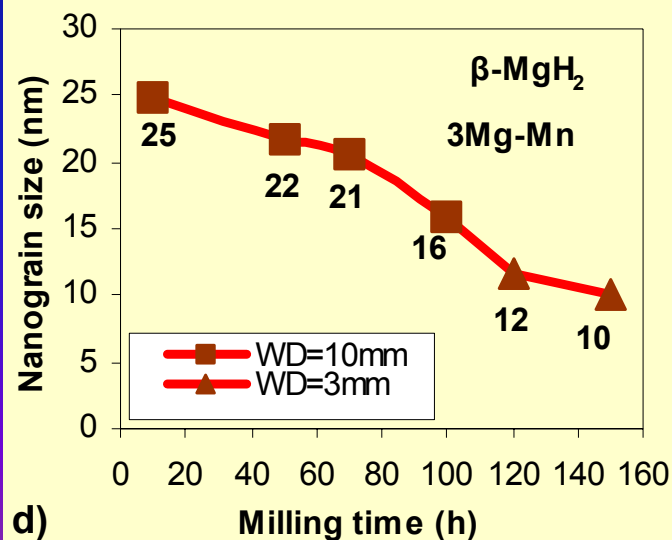
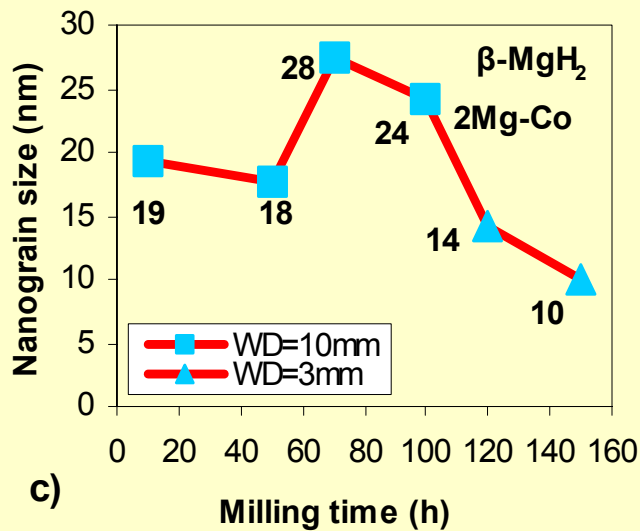
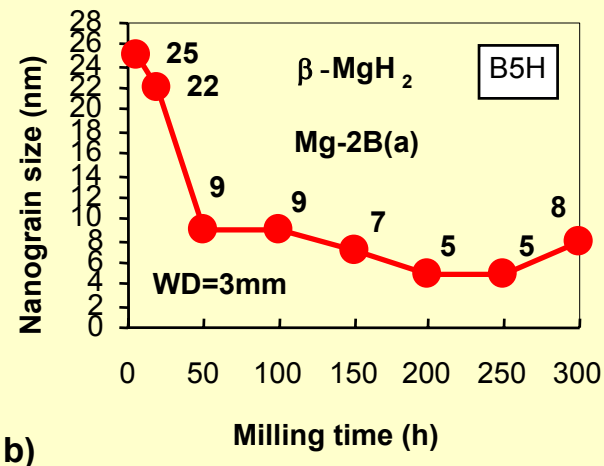
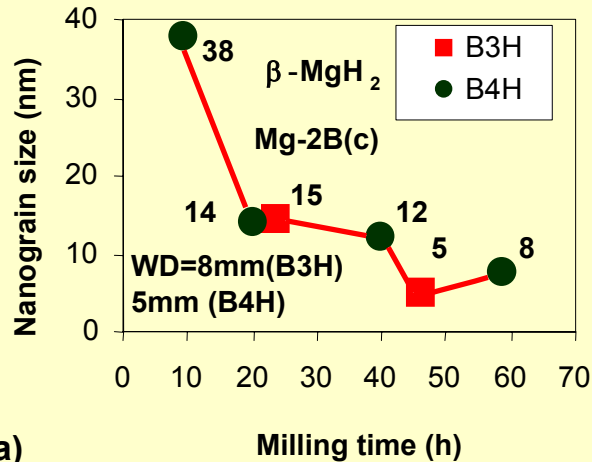
# RESULTS-XRD intensities vs. milling time (cont.)



- **Mg-2B(a)-complete consumption** of Mg to form  $\beta$ -MgH<sub>2</sub> (at 50h)
- **Mg-2B(c)-incomplete consumption** of Mg to form  $\beta$ -MgH<sub>2</sub>
- **Partial amorphization (?)** of  $\beta$ -MgH<sub>2</sub> after 50 and 20h of CRMA, respectively

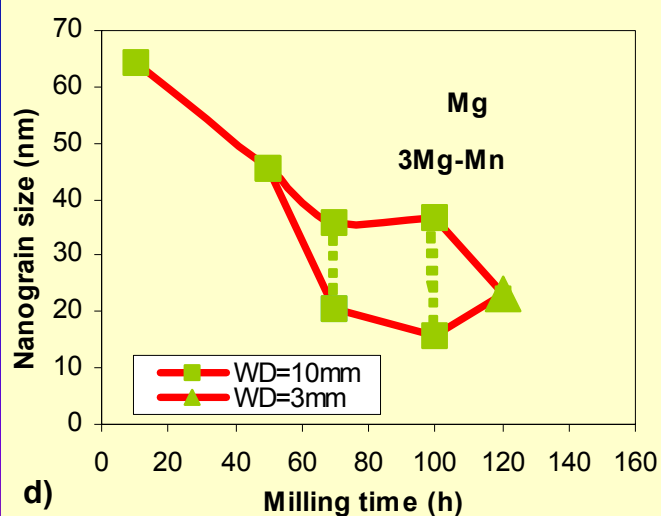
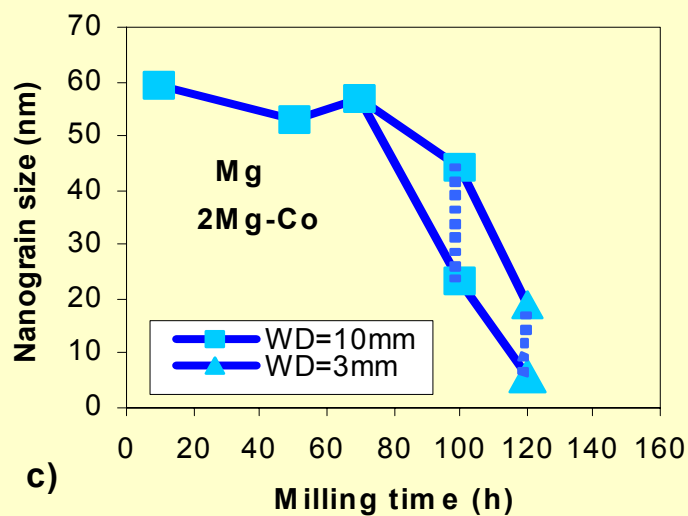
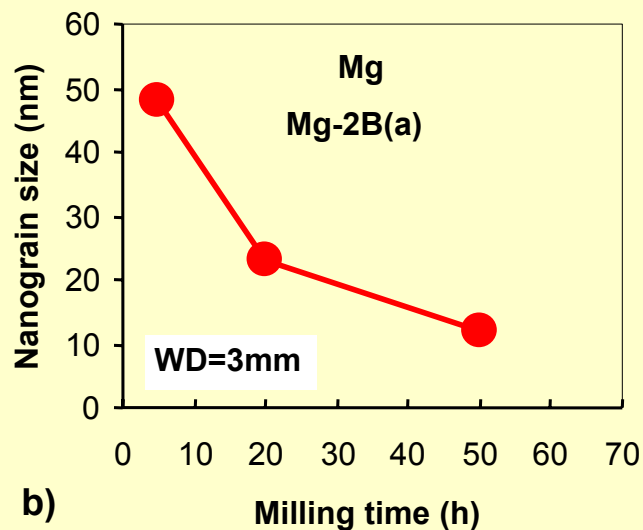
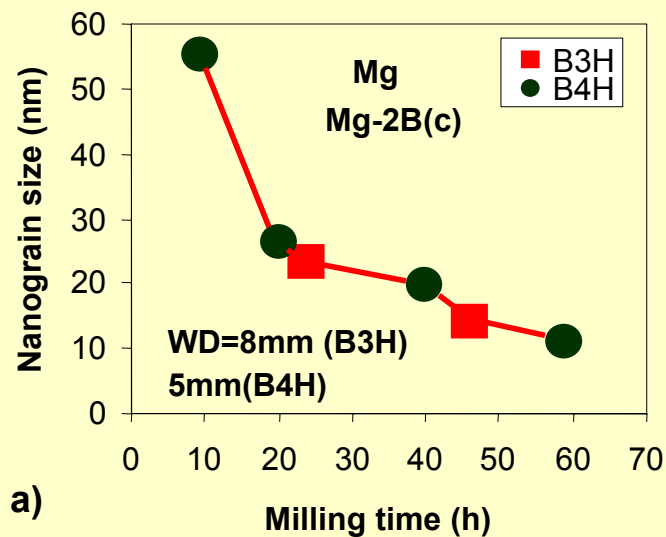


# RESULTS-Nanostructured $\beta$ -MgH<sub>2</sub> hydride



Principal  
hydride in  
**2Mg-Co**,  
**3Mg-Mn** and  
**Mg-2B** is  
**nano- $\beta$ -MgH<sub>2</sub>**

# RESULTS-Nanostructured Mg

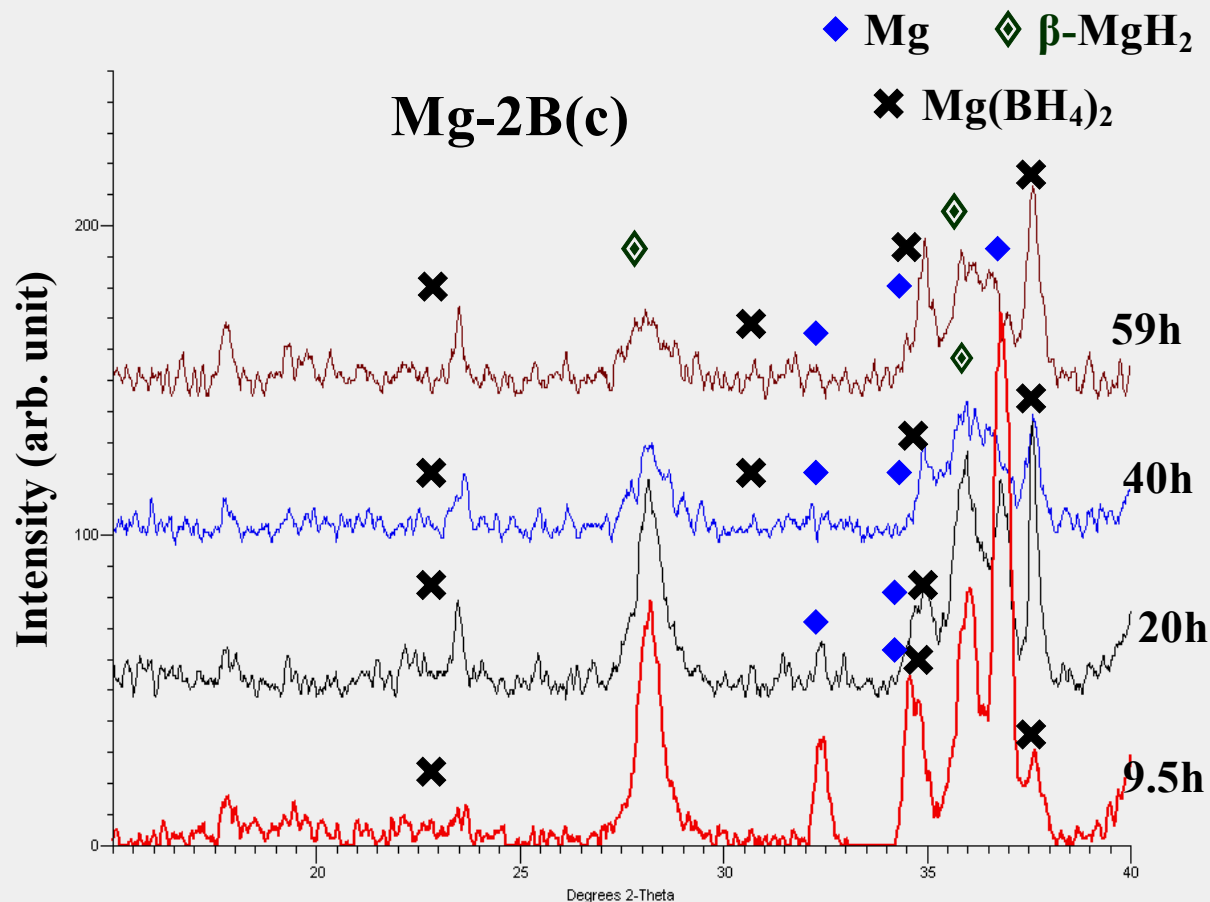


Nanocomposite  
 $\text{Mg} + \beta\text{-MgH}_2 + [\text{Mg}(\text{BH}_4)_2?]$   
 up to 50-60h of milling

Nanocomposite  
 $\text{Mg} + \beta\text{-MgH}_2 + (\text{remnant Co; Mn})$   
 up to 120h of milling



# RESULTS-Nanostructured $\text{Mg}(\text{BH}_4)_2$ in $\text{Mg-2B(c)}$ system

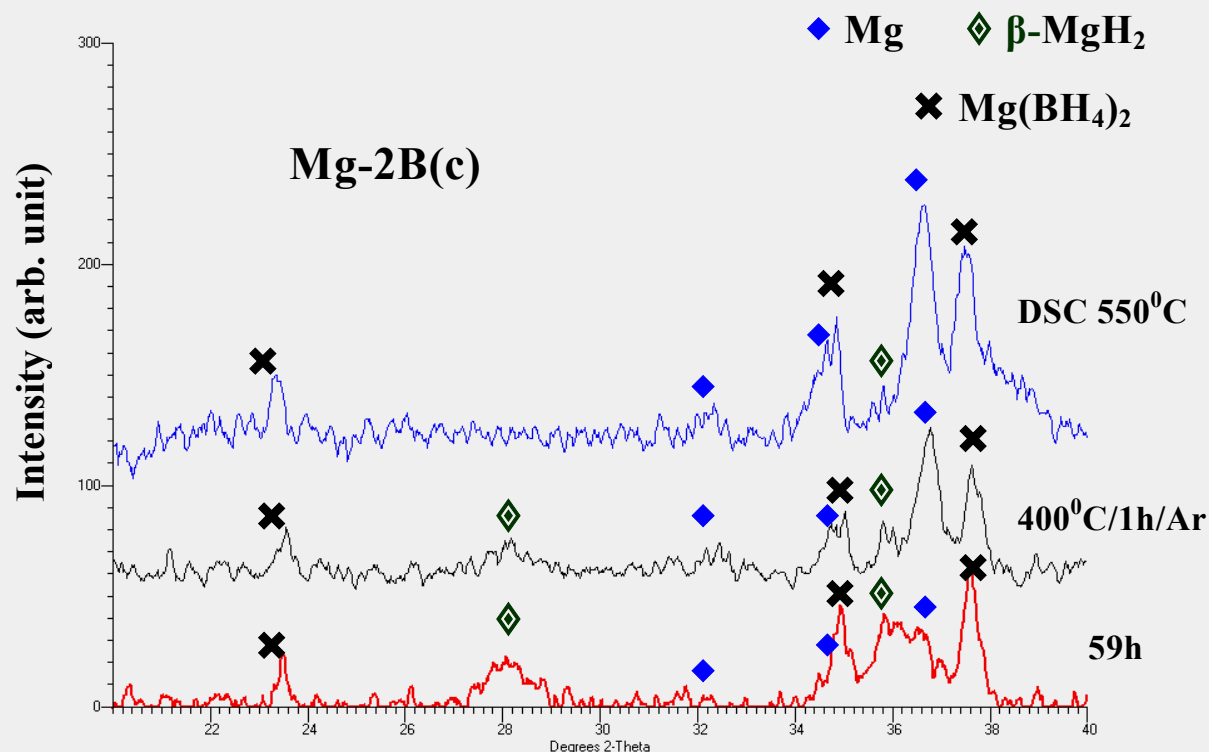


✕ shows the exact peak position for  $\text{Mg}(\text{BH}_4)_2$  according to JCPDS Powder Diffraction File No.26-1212

[similar peaks but weaker also in XRD from  $\text{Mg-2B(a)}$ ]

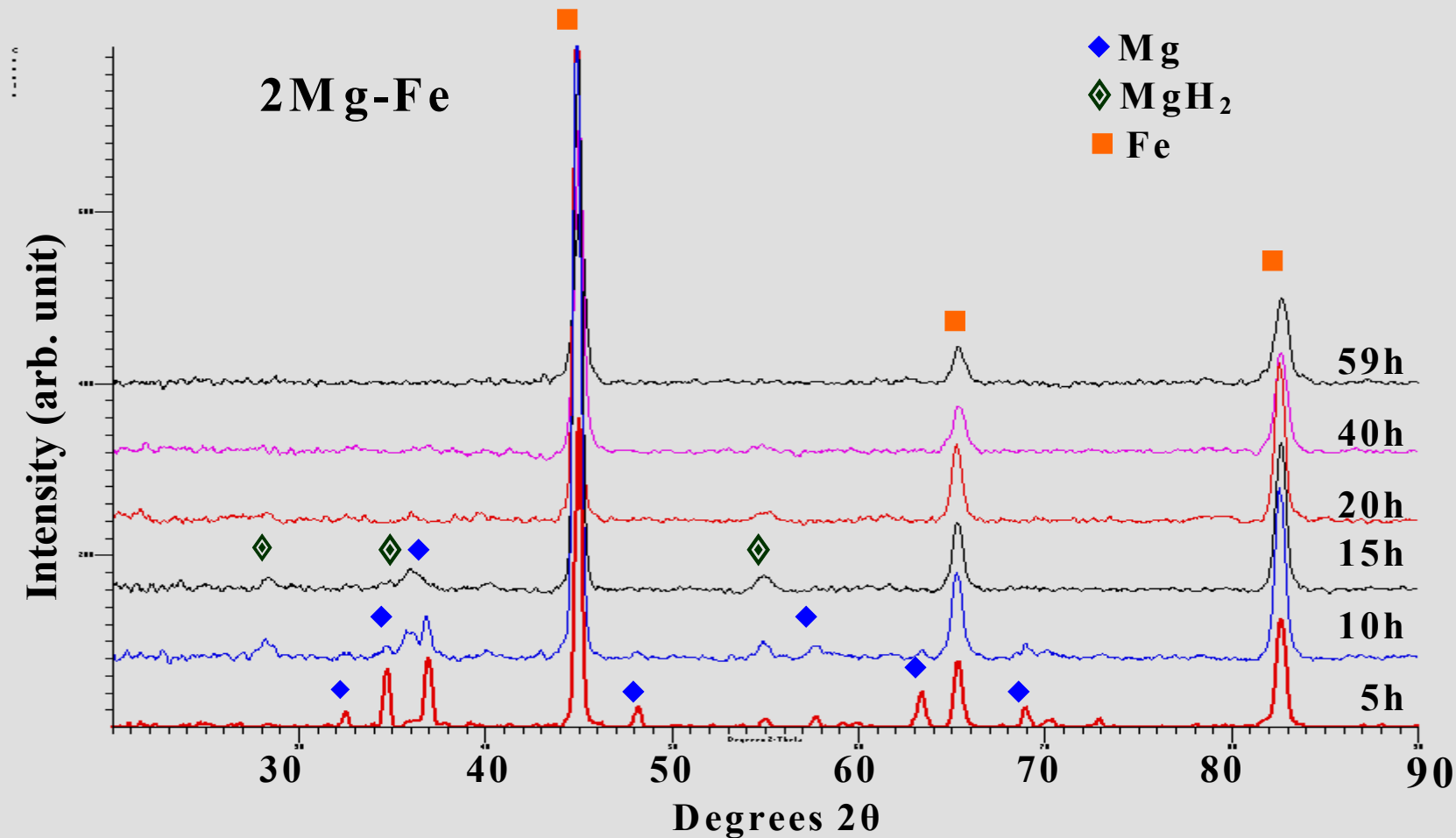


# RESULTS - Nanostructured $\text{Mg}(\text{BH}_4)_2$ –XRD after thermal analysis

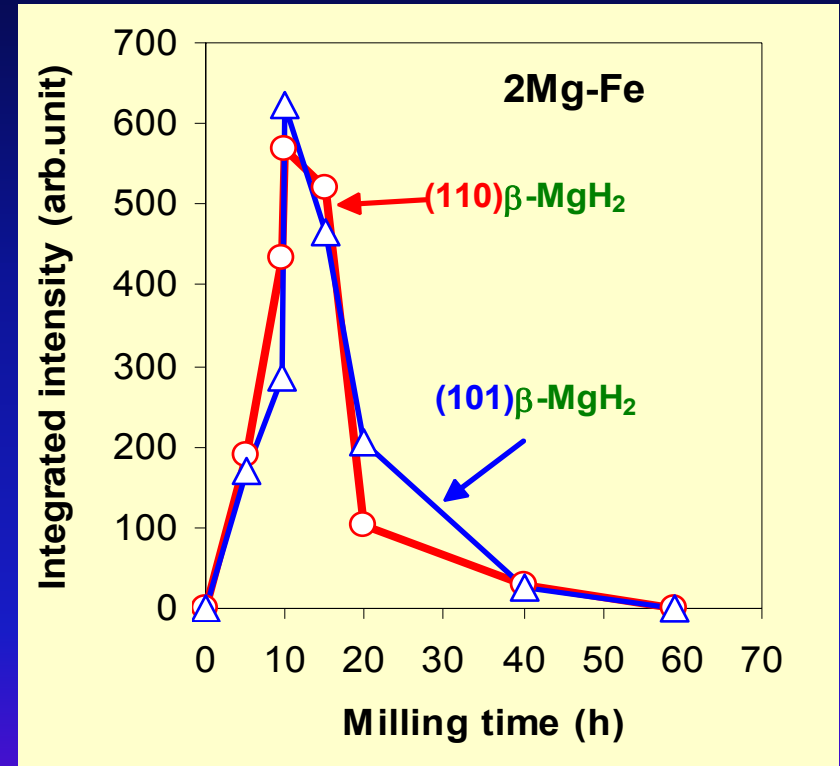
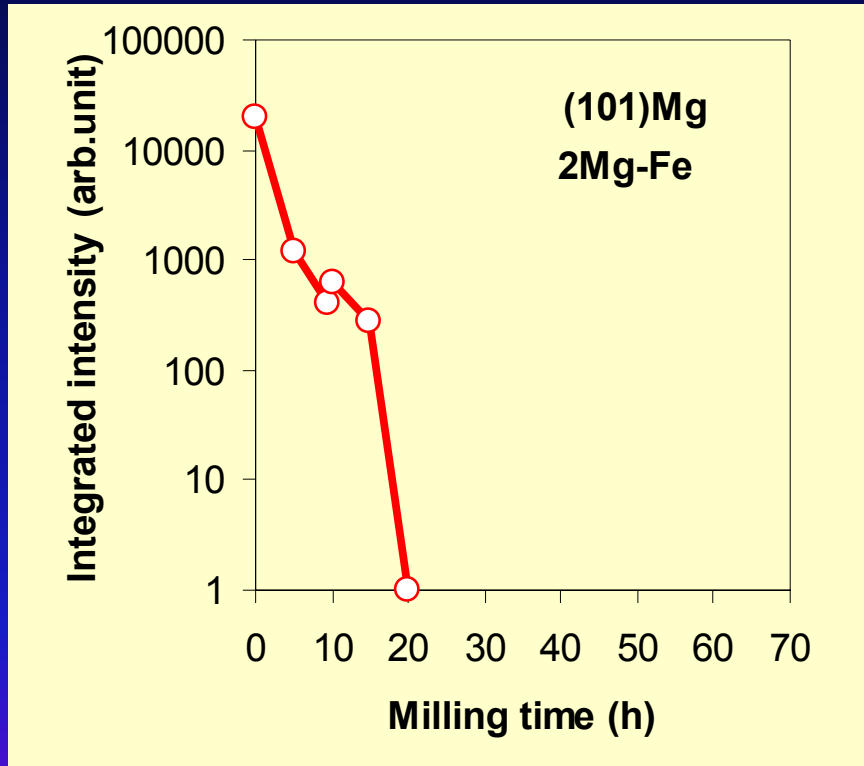


Thermally  
stable  
hydride?

# RESULTS - Amorphization in the 2Mg-Fe-H system - XRD pattern

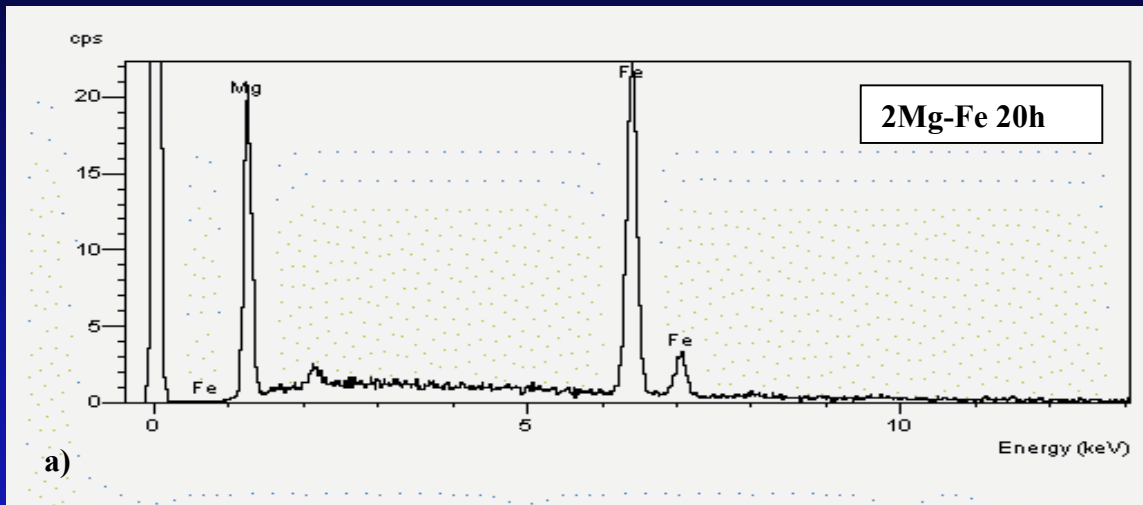


# RESULTS - Amorphization in the 2Mg-Fe-H system - XRD intensities



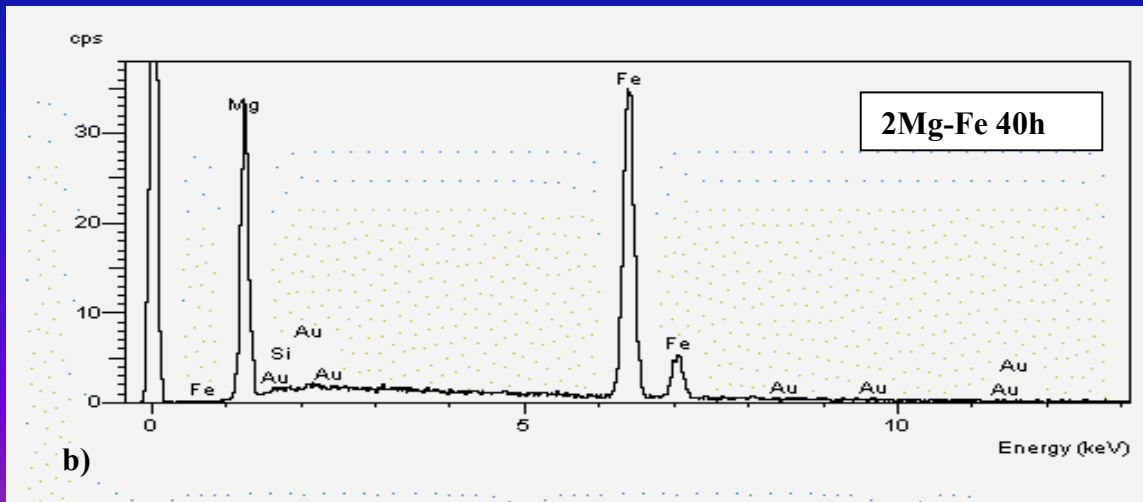
Amorphization of Mg and β-MgH<sub>2</sub>!

# RESULTS - **Amorphization** in the **2Mg-Fe-H** system – **Qualitative EDS**

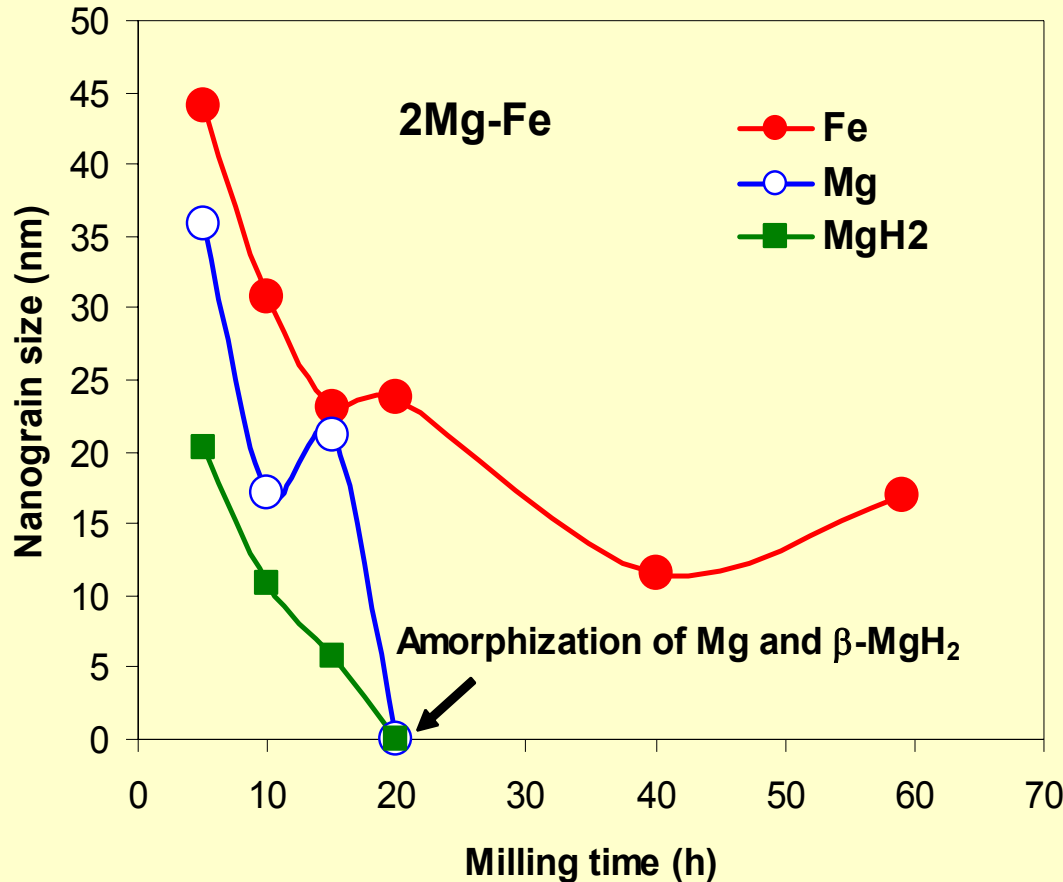


Mg peak clearly seen in EDS profile but absent in XRD:

**Mg exists in the amorphous state**



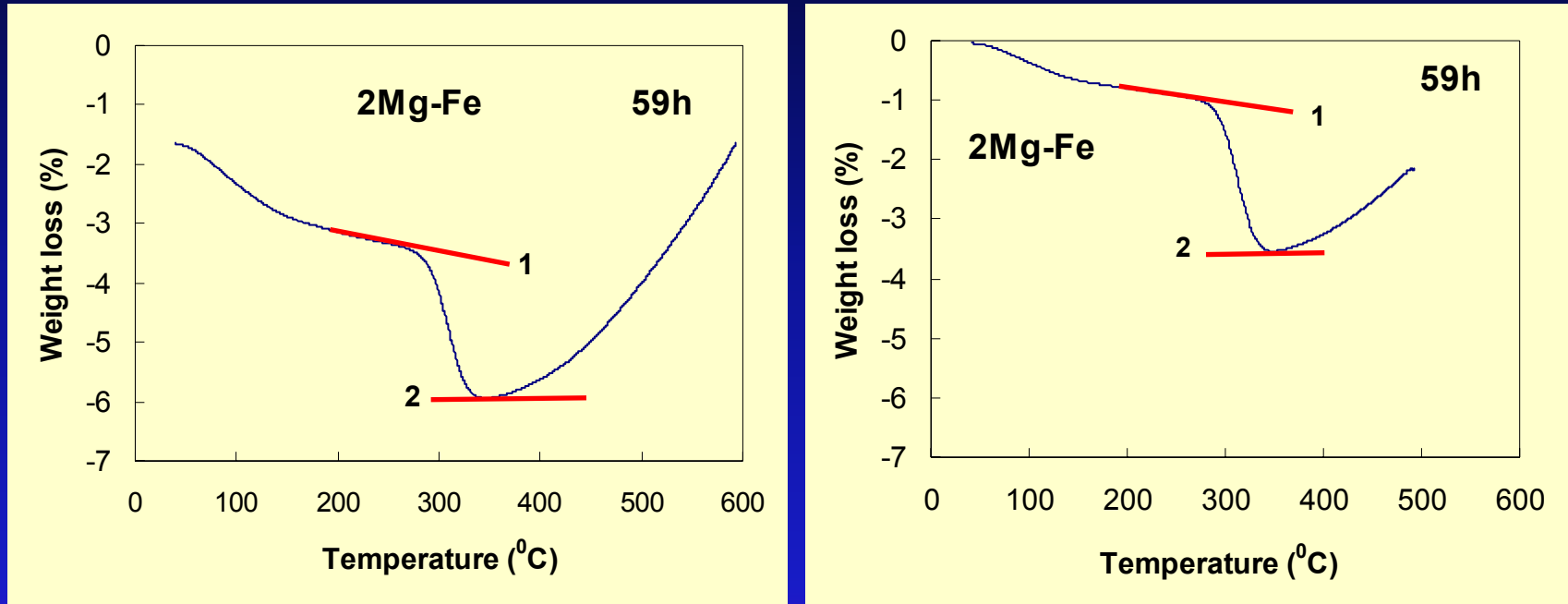
# RESULTS - Amorphization in the 2Mg-Fe-H system - Nanograin size/nanocomposite



Oleszak&Shingu,Mater.  
Sci.Forum 235-238  
(1997) 91-96

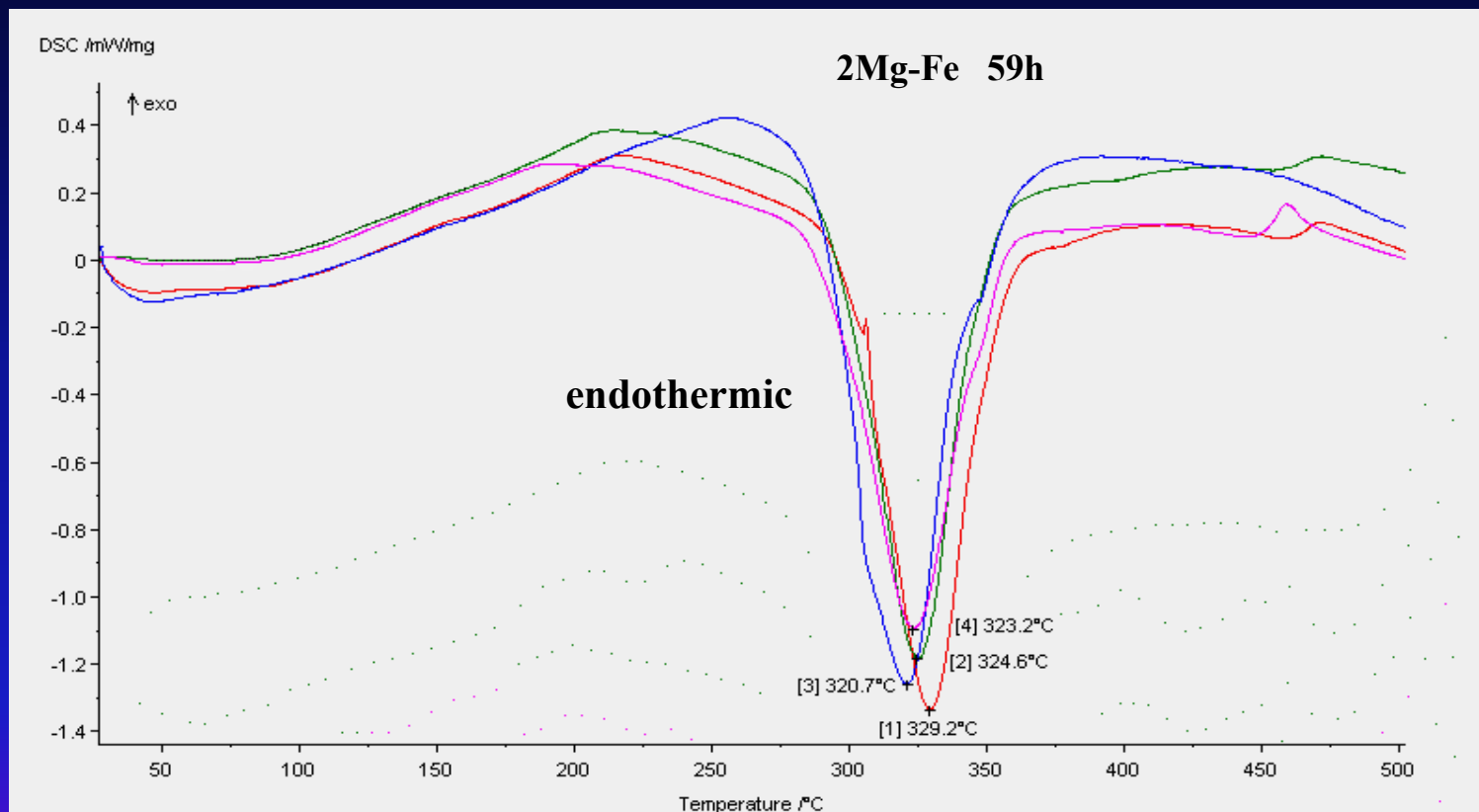
Critical average  
nanograin size  
favorable to the  
formation of  
amorphous phase is on  
the order of **~10 nm**

# RESULTS - Amorphous hydrides in the 2Mg-Fe-H system – Thermal behavior-TGA



Desorption from amorphous hydrides: range 2.21-4.16wt% between tangent lines 1 and 2 from all TGA runs

# RESULTS - Amorphous hydrides in the 2Mg-Fe-H system – Thermal behavior-DSC



Peak temperature range: 320.7 -329.2°C – agrees well with TGA

## RESULTS - Amorphous hydride in the 2Mg-Fe-H system – stoichiometric formula

Based on the results of desorbed hydrogen observed in TGA runs which was in the range 2.21-4.16wt% the stoichiometric formula of the amorphous hydride can be estimated as  $\text{MgH}_{0.6-1.1}$ . The hydrogen-to-metal ratio in this formula is nearly 1 which implies that the amorphous hydride has a *metallic* character. This is in excellent agreement with Orimo et al [Acta mater. 45 (1997) 2271-2278] who reported that amorphous hydrides in various systems have the hydrogen-to-metal ratio  $\sim 1$  and metallic character.



## SUMMARY/CONCLUSIONS

1. A principal nanostructured hydride formed in 2Mg-Co, 3Mg-Mn and Mg-2B mixtures is  $\beta\text{-MgH}_2$ ; no  $\text{Mg}_2\text{CoH}_5$  and  $\text{Mg}_3\text{MnH}_7$  complex hydrides have been formed during CRMA under *shearing* mode despite a profound **nanosctructurization** of elemental species in the mixture (Question: *why no formation of complex hydrides has occurred?*)
2. XRD peaks close to the peaks from  $\text{Mg}(\text{BH}_4)_2$  are observed on the scans from the **Mg-2B(crystalline)** mixture and on the scans (but weaker) from the **Mg-2B(amorphous)** mixture

## SUMMARY/CONCLUSIONS (cont.)

3. In the **2Mg-Fe** mixture there is initially a gradual *nanostructurization* of the **Mg** and  **$\beta$ -MgH<sub>2</sub>** phases followed by *amorphization* of both phases with increasing milling time. Eventually the amorphous hydride, possibly with the stoichiometric formula **MgH<sub>0.6-1.1</sub>**, is being formed; no formation of complex hydride Mg<sub>2</sub>FeH<sub>6</sub> is observed

*(Question: why no formation of Mg<sub>2</sub>FeH<sub>6</sub> has occurred (successfully synthesized by some other researchers) and instead an amorphous hydride has been formed ?*

# **ACKNOWLEDGEMENT**

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Natural Sciences and Engineering Research  
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acknowledged**